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The Liquid-Liquid Extraction of Alkaline Earth Metals with TTA (2-Thenoyltrifluoroacetone)

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The liquid-liquid extraction of alkaline earth metals was investigated with a TTA-MIBK solvent and a NH_4OAc-AcOH-NH_4OH aqueous solution in the presence of relatively large amounts of the metals. The extractability of the metal ions was in the decreasing order of magnesium, calcium, strontium and barium, while their distribution ratios were too close to one another for them to be separated from each other. Critical studies were made on several factors affecting the distribution of each metal, such as the amount of metal in the aqueous solution, the concentration of TTA in the organic solvent, and the pH of the solution. It was noticed that the concentration of TTA in MIBK played a principal role in this extraction and that the log D-log(TTA) relation was shown as a curve, not a straight line. The relation in other similar cases had usually been shown as a straight line, but the new results were obtained by compensating pH-change, the extent of which was variable with the concentration of TTA in the system. Among the metal ions, calcium and magnesium could be separated from each other by carrying out the extraction from their solution in the presence of EDTA. A further extention of this extraction to a reversed-phase partition chromatography will be undertaken and reported on in another paper.

The chelating agent 2-thenoyltrifluoroacetone (usually abbreviated as TTA) has proved to be a valuable reagent for the solvent extraction of many metal ions. It has the property of accomplishing the extraction from stronger acid solutions than other chelating agents. Thus, there is a wide range of metal ions that may be extracted without interference from hydrolysis. A considerable amount of work has been done on the use of TTA[1] alone or with other chelating agents.[2] However, there have been few works on the extraction of alkaline earth metal ions except for the determination of the stability constant of their chelates with TTA.[3] Khym, Tompkins and Cohen[4] have reported the separation of the calcium-45 produced by the Sc(d, 2p) reaction from the target by solvent extraction with 0.5 M TTA in benzene from a solution of pH 9. Kiba and Mizukami[5] have studied the rapid separation of radioactive strontium by solvent extraction with 0.05 M TTA in methyl isobutyl ketone (abbreviated as MIBK) from a solution of pH 8. Although TTA was believed to cleave to trifluoroacetic acid and acetylthiophen when the pH of its aqueous solution was in excess of 9,[6] their intuitive choice of the solvent surmounted a difficulty of using TTA in a basic medium, for MIBK was later proved as to be a good retardent for the decomposition of TTA,[7] as well as a good polar solvating agent to facilitate the chelate formation and extraction. After this study, alkaline earth metals and heavier alkali metals such as cesium became the objects of quantitative extraction with TTA in MIBK from their aqueous solutions of higher pH values, especially in the preparation of radio-isotopes, the processing of irradiated reactor fuel, and the analysis of fission products.[8] However up to the present there have been no systematic studies of the liquid-liquid extraction of alkaline earth metals with TTA-MIBK in relatively large amounts of the metals.

The present author studied critically the extraction from aqueous solutions over a wide range of pH values, and determined the distribution ratio of each individual ion with relation to the concentration of TTA in the solvent and the pH of the aqueous phase. It was noticed that the distribution ratio between two phases varied remarkably with the concentration of TTA in the organic phase, and that the extraction mechanism is not as simple as it had been considered to be. As a result, the distribution ratios of the metals are too close together for them to be separated easily. The author aims to separate these metal ions by later extending this extraction method to the reversed-phase partition chromatography, which will be described in another paper.

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Experimental

Reagents and Apparatus. — *TTA (2-Thenoyltrifluoroacetone)*.—Dotite TTA, prepared by the Dōjindō Research Laboratories, was used without further purification. It was dissolved in MIBK (methyl isobutyl ketone) of an analytical reagent grade to make a 0.2 M TTA-MIBK solution in most cases.

Buffer Solution.—A buffer solution consisting of ammonium acetate - ammonia - acetic acid was employed to keep constant the pH of the aqueous solution. In consideration of its buffer capacity, a 6 M-solution was usually employed for adding to the sample solution, and the final concentration of the buffer solution was made 3 M by diluting the test solution to twice the volume of the initial buffer solution. Sometimes a 1.0 M buffer solution was also used to make the final concentration of the test solution 0.5 M.

Salt Solution.—Barium chloride dihydrate, strontium nitrate tetrahydrate, calcium nitrate tetrahydrate, and magnesium chloride hexahydrate, all of analytical grades, were dissolved in water to make solutions containing 10^4 p. p. m. of the metal ion. The concentration of each solution was standardized by titration with EDTA (ethylenediaminetetraacetic acid disodium salt). The stock solutions thus prepared were diluted with water to suitable concentrations before use.

Radioactive strontium-90 - yttrium-90 as nitrate and barium-140 - lanthanum-140 as chloride were employed in order to examine their behavior in the extraction, after their daughter nuclides had been separated by the usual method.

EDTA Solution.—Analytical-grade disodium salt of ethylenediaminetetraacetic acid (Dotite 2 Na) was dissolved in water to make a 0.01 M solution, the concentration of which was then standardized with standard calcium carbonate.

Buffer Solution of pH 10.—The buffer solution used for titration by EDTA was prepared by dissolving 7 g. of ammonium chloride in 57 ml. of aqueous ammonia and then diluting it to 100 ml.; it was adjusted to pH 10 by adding an ammonium chloride solution or aqueous ammonia.

Eriochrome Black T, the indicator, and a 0.1 M magnesium-EDTA solution were prepared as usual.

Separating Funnel.—A 85 ml., spindle-type separating funnel was used.

pH Meter.—A pH meter with a glass electrode and a saturated calomel electrode, Model M-3 Horiba Manufacturing Co., was employed.

Flame Photometer. — A spectrophotometer, Hitachi Model EPU-2A, provided with an accessory flame burner, H-2, was used to determine the quantity of metal ions in a solution, using hydrogen gas as the fuel.

Radioactivity Counter.—A G-M counting set of the Kōbe Kōgyō Co., consisting of a No. 131-G-M tube and a "100 scalor," was used for β-counting.

Shaker.—The shakng of the separating funnel was effected by a vertical electric shaker, Iwaki Model 3, operating at 300 strokes per minute.

Experimental Procedure. — In the separating funnel 10 ml. of a 0.2 M TTA-MIBK solution, 5 ml. of a sample solution and 5 ml. of a 6 M buffer solution were put together. The funnel was then shaken for ten minutes with the electric shaker. After the two phases had separated the aqueous solution was taken out through the stem and its pH was measured. The sample solution adhering to the glass electrode of the pH meter and to the inside wall of the funnel was washed down into a beaker. On the other hand, the organic phase remaining in the funnel was treated with 5 ml. of 1 M hydrochloric acid in order to back-extract the metal ion in the organic phase. The back extraction was repeated twice, and the acid washing was submitted to the determination of the metal ions contained in the organic phase. The original aqueous phase was also submitted to the determination, according to the following methods.

Titration Method.—The aqueous solution was nearly neutralized with a 1 M sodium hydroxide solution or 3 M aqueous ammonia, and 2 ml. of a buffer solution with a pH of 10 was added; then 2 ml. of a magnesium-EDTA solution was pipetted into the solution. The solution was titrated with a 0.01 M EDTA solution and two or three drops of a BT indicator solution. The acetate ion, which interferes with the clear exhibition of this color change, should be completely eliminated by evaporating the aqueous solution to dryness with a strong acid before the titration.

Flame Photometry. — The original aqueous phase contained various amounts of acetate, so it was difficult to re-establish the same conditions in a series of reference solutions and so draw the working curve. Therefore, the back-extract was submitted to flame photometry. However, in the solution some acetic acid, ammonia and TTA - methyl isobutyl ketone were present, together with the metal ion to be tested. These substances were removed by the following treatment before the flame-photometric determination. A half-volume of ethyl ether was added to the solution in a separating funnel, and the contents shaken for a while; then the aqueous phase was transferred into another funnel and shaken with ether again. The aqueous solution separated from ether was warmed to 50°C, and air was passed through the solution for about thirty minutes in order to expel the ether. Then the solution was submitted to the determination. As references for the determination a series of solutions were prepared containing definite amounts of the respective metals in 1 N hydrochloric acid.

Results and Discussion

Preliminary Experiments.—*The Behavior of Individual Ions*.—In order to examine the behavior of individual ions in larger amounts, some preliminary experiments were undertaken under the same conditions as had been done in its trace scale by Kiba and Mizukami.⁵⁾ In a separating funnel there were placed together 5 ml. of a 1.0 M buffer solution of pH 8.0, 5 ml. of a 0.02 M solution of the metal ion, and 10-ml. of a TTA-MIBK solvent of varying concentrations, from 0.05 M to 0.5 M. The recovery of each ion in the organic phase is shown in Fig. 1, from which it may be found that the percent extraction decreases in the order of magnesium, calcium, strontium and barium, and increases with the concentration of TTA in methyl isobutyl ketone. Extraction was also carried out with strontium and barium in varying amounts from a trace to 0.005 M; the recovery is shown in Figs. 2 and 3.

In each case the increase in the concentration of TTA promoted the extraction of metal ions, and the larger the quantity of metal ion present, the lower was the percentage of extraction. When the quantity of metal ions was minute, methyl isobutyl ketone containing 0.2 M or more of TTA was very useful in effecting a satisfactory recovery of the metal. The extraction behavior was much the same in these four metals, as is shown by the closeness of the extraction curves in Fig. 1.

The Use of a Mixed Solvent.—Because of the similar behavior of the metal ions, the separation from one another seemed to be very difficult. Therefore, the mixed solvent was used in an attempt to effect a separation of the metals. Ten milliliters of a mixed solvent consisting of 0.1 M TTA - benzene and 0.1 M TTA - MIBK in various ratios was used for extraction from a solution composed of 5 ml. of a 1.0 M buffer solution of pH 8.0 and 5 ml. of a 0.02 M solution of metal ions. The results obtained with mixed solvents of various compositions are shown in Fig. 4, which reveals that though the percentage extraction of each metal increases with the volume of TTA-MIBK, no better separation from one another can be expected. It also reveals that benzene does not play any role in the attainment of selectivity. Thereafter, MIBK was exclusively employed in this method.

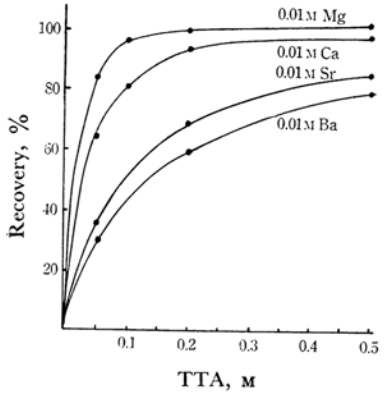

Fig. 1. Recovery of metal ions from 10 ml. of aqueous phase consisting of 0.5 M buffer solution of pH 8.0 and 0.01 M solution of metal ion by extraction with 10 ml. of MIBK containing various amounts of TTA.

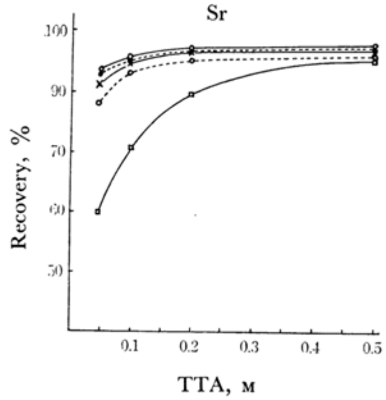

Fig. 2. Recovery of strontium by 10 ml. of MIBK containing various amounts of TTA from 10 ml. of aqueous phase consisting of 0.5 M buffer solution of pH 8.0 containing various amounts of strontium.

○—○ Carrier free ●--● 0.0001 M
×—× 0.0005 M ○--○ 0.001 M
□—□ 0.005 M

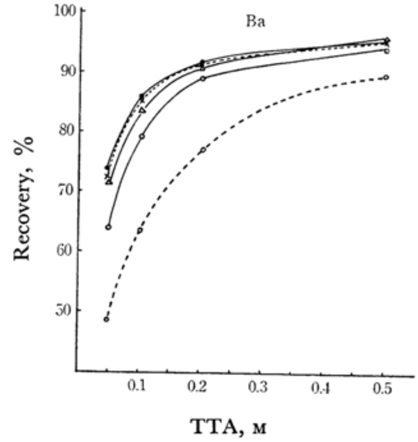

Fig. 3. Recovery of barium by 10 ml. of MIBK containing various amounts of TTA from 10 ml. of aqueous phase consisting of 0.5 M buffer solution of pH 8.0 containing various amounts of barium.

●—● Carrier free ×--× 0.0001 M
△—△ 0.0005 M ○—○ 0.001 M
○--○ 0.005 M

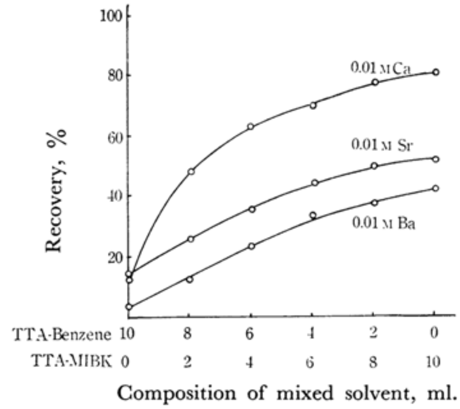

Fig. 4. Recovery of metal using mixed solvent.
Aqueous phase: 10 ml. of 0.5 M buffer solution of pH 8.0
Organic phase: 10 ml. of mixed solvent of 0.1 M TTA - MIBK and 0.1 M TTA - Benzene

The Change in pH During Extraction.—When a 1.0 M buffer solution was used in an aqueous phase, the pH, which was 8.0 initially, became 6.8 after the extraction. Since TTA can be considered to be a weak acid, its dissolution into the aqueous phase during the extraction and the release of protonized hydrogen from it by the metal ion may have caused the increase in hydrogen ions in the aqueous phase. In order to keep the pH nearly constant during the extraction, a 6 M buffer solution was preferred because of its large buffer capacity. In the subsequent experiments 5 ml. of the buffer solution was taken and diluted to 10 ml. with the sample solution and water in order to make the buffer concentration in the aqueous phase 3 M. The concentration of TTA in MIBK was also kept at 0.2 M in the subsequent experiments.

The Mechanism of Extraction.—The equation for the extraction of a metal ion with the charge $+z$, M^{z+}, and with a monobasic chelating agent, HT, can be simply written as:

$$M^{z+}{}_{(a)} + z\mathrm{HT}_{(o)} \rightleftharpoons \mathrm{MT}_{z(o)} + z\mathrm{H}^{+}{}_{(a)}$$

where the subscripts a and o refer to the aqueous and organic phases respectively. A thermodynamic extraction constant for this process can be written most simply as:

$$K = (\mathrm{MT}_z)_o(\mathrm{H}^+)_a^z/(\mathrm{M}^{z+})_a(\mathrm{HT})_o^z$$

and:

$$K = D(\mathrm{H}^+)_a^z/(\mathrm{HT})_o^z$$

where D is the extraction coefficient (the total concentration of metal in the organic phase/the total concentration of metal in the aqueous phase).

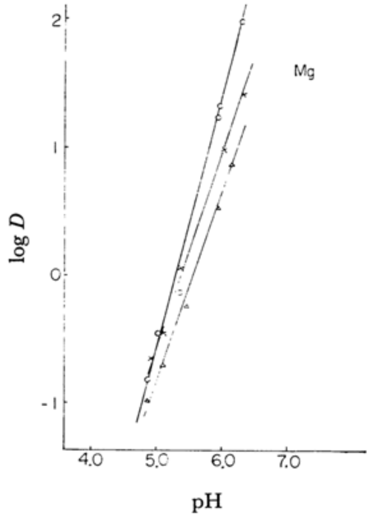

Fig. 5. Dependence of distribution ratio, D upon the pH of the solution in case of magnesium.
Aqueous phase: 3 M Buffer solution
Organic phase: 0.2 M TTA - MIBK
○ 0.125 mmol./10 ml. × 0.25 mmol./10 ml.
△ 0.50 mmol./10 ml.

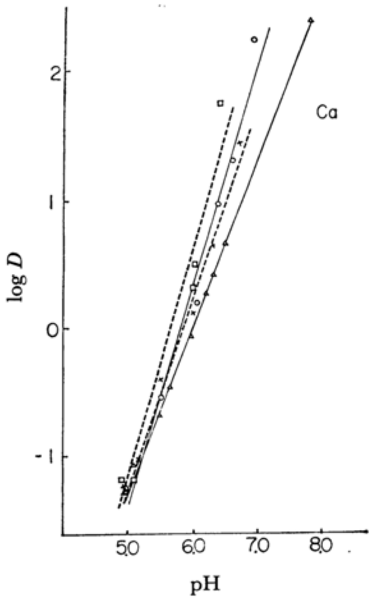

Fig. 6. Dependence of distribution ratio, D upon the pH of the solution in case of calcium.
Aqueous phase: 3 M buffer solution
Organic phase: 0.2 M TTA - MIBK
☐ 0.031 mmol./10 ml. ○ 0.125 mmol./10 ml.
× 0.252 mmol./10 ml. △ 0.508 mmol./10 ml.

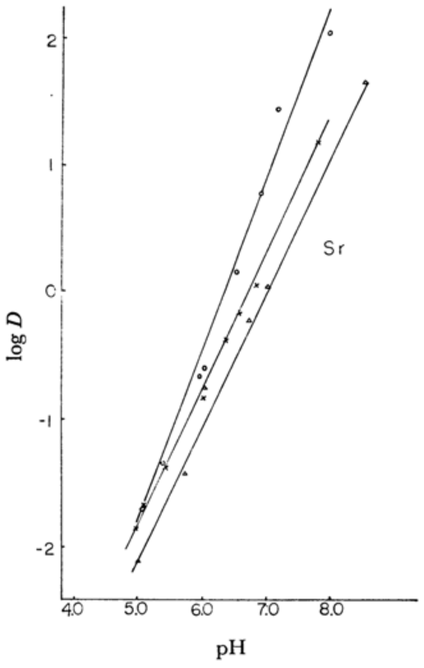

Fig. 7. Dependence of distribution ratio, D upon the pH of the solution in case of strontium.
Aqueous phase: 3 M buffer solution
Organic phase: 0.2 M TTA - MIBK
○ 0.143 mmol./10 ml. × 0.573 mmol./10 ml.
△ 0.286 mmol./10 ml.

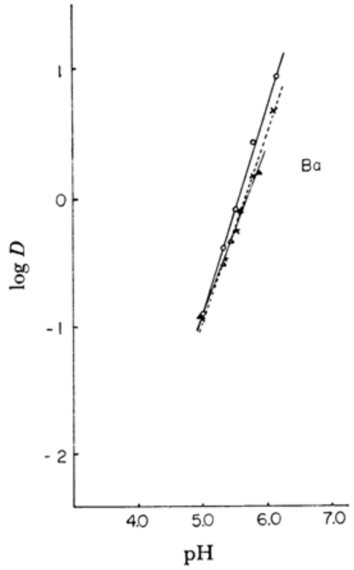

Fig. 8. Dependence of distribution ratio, *D* upon the pH of the solution in case of barium.

Aqueous phase: 3 M buffer solution
Organic phase: 0.2 M TTA - MIBK
○ 0.125 mmol./10 ml. × 0.25 mmol./10 ml.
△ 0.498 mmol./10 ml.

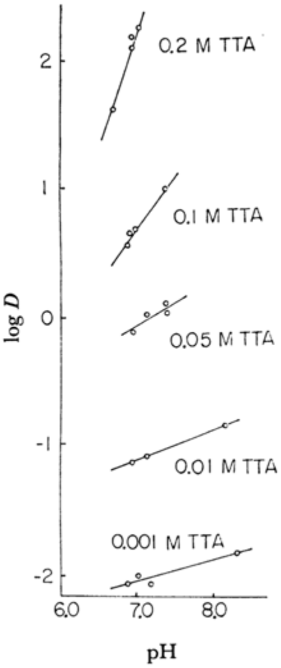

Fig. 9. Dependence of distribution ratio, *D* upon the pH of the solution.

Aq. phase: 3 M buffer solution containing 0.125 mmol. of calcium
Org. phase: MIBK containing varying amounts of TTA

D can also be written as:

$$D = K(\mathrm{HT})_{\mathrm{o}}^{z}/(\mathrm{H}^{+})_{\mathrm{a}}^{z} \qquad (1)$$

Therefore, the distribution ratio depends on the activity of both the chelating agent and the hydrogen ions. The values of *D*, determined in various concentrations of the chelating agent while the pH is kept constant, and at varying pH values at a definite concentration of the chelating agent, may clarify the extraction mechanism.

First the dependence of *D* on the pH of an aqueous solution after the extraction was examined by the following experiments. The distribution ratios were estimated in a series of extractions between 10-ml. portions of organic and aqueous phases, the former being 0.2 M TTA - MIBK and the latter consisting of various amounts of a metal ion in a 3 M buffer solution of varying pH values. The relations between log*D* and pH after the extraction are shown as straight lines having slopes of unity to two for magnesium, calcium, strontium and barium, respectively, in Figs. 5, 6, 7 and 8. The slope becomes sharper as the quantity of the metal ions decreases and as the stability of the metal chelate increases.[1] The dependence of *D* on the concentration of TTA in methyl isobutyl ketone was also examined in the extraction between 10-ml. portions of organic and aqueous phases, the former being MIBK containing various amounts of TTA, and the latter consisting of 5 ml. of a 0.025 M solution of calcium ion and 5 ml. of a 6 M buffer solution of varying pH values. The results are summarized in Fig. 9, in which the pH noted is, of course, that of the aqueous phase after the extraction.

Next, the author attempted the extraction at a constant pH value of 7.0 of the aqueous phase and at the constant concentration of calcium of 0.125 mmol. between 10 ml. of the aqueous phase and 10 ml. of MIBK containing varying amounts of TTA. However, the author failed in the attempt to make the pH of the solution exactly 7.0 after each extraction, since the pH of the aqueous phase was liable to be made lower by mere contact with the organic phase, probably because of the partial transfer of the TTA from the organic to the aqueous phase. Even when a buffer solution with a higher capacity, such as a 6 M solution, is used, the pH of the aqueous solution cannot be guaranteed to remain strictly constant. Moreover, when an organic solvent containing a still larger amount of TTA is employed, the distribution of calcium is enormously affected by even a slight change in the pH, as is shown in Fig. 9. The proper distribution ratio should be estimated at the constant pH, but it is difficult to maintain the constant pH over all the estimation of log *D* - log(TTA). Therefore, the relation of the distribution ratio to the concentration of TTA at pH 7.0 was constructed from the data in Fig. 9. A noteworthy fact was thereby found about the extraction mechanism. As Fig. 10 shows, the concentration of TTA, noted as (TTA) in the figure, has the relation with the distribution ratio given in the curve of log D vs. log(TTA). The curve seems to illustrate the true behavior of the extraction at pH 7.0. Nevertheless, a number of researchers who investigated the extraction of the TTA-chelates of other metals have described how the relation between log D and log(TTA) is usually represented by a straight line with a slope of an integral value, the integer being the number of TTA molecules attached to the metal. In many cases they seem to have overlooked the facts that the pH of the aqueous solution is lowered not only by the hydrogen ion exchanged with the metal, but also by the dissociation of TTA in the aqueous phase; that a lowering of the pH is remarkable when the concentration of TTA is high, and that, therefore, the higher the concentration of TTA, the larger the decrease in the extent of the distribution ratio. Such a change in the pH will be slight in an acidic solution, but it will be remarkable in a neutral or alkaline solution.

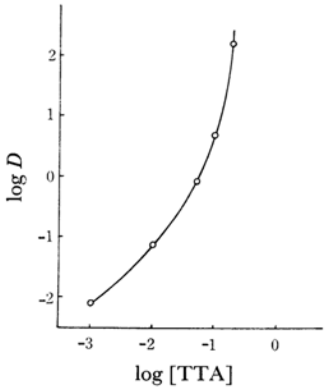

Fig. 10. Dependence of log [TTA] at pH 7.0, same data as in Fig. 9.

The curve drawn by the present author appears as a smooth one in Fig. 10, but it is suspected that it is really composed of a large number of short lines, with their slopes increasing from unity to large integers. This suggests that various species of metal-chelate are formed with the increase in the concentration of TTA in the organic phase. When the concentration of TTA is large, the number of TTA radicals attached to the calcium atom increases and, as a matter of fact, the distribution of the metal into the organic phase is enhanced. In addition, the distribution of metal usually depends upon the following factors: the time required for the attainment of equilibrium, the temperature, the kind and concentration of the metal ion and of the chelating agent, the pH of the aqueous phase, the other chelating agents present, the adduct-forming agent, and the organic solvent used.9)

The extraction between an aqueous phase containing a divalent ion as calcium and an organic phase containing TTA can be written as follows:

$$M^{2+}{}_{(a)} + 2HT_{(o)} \rightleftharpoons MT_{2(o)} + 2H^+{}_{(a)} \qquad (2)$$

$$D = K(HT)_o^2/(H^+)_a^2 \qquad (3)$$

Therefore, D is inversely proportional to the square of (H^+). As has been described above, the author has found that the relation between log D and pH is linear, with the slope between unity and two. Therefore, Eq. 3 can explain the phenomenon where the slope is two, but not where it is unity. Similar behavior of alkaline earth metals has already been cited in the description by Cerrai et al.,10) who investigated the liquid-liquid extraction of alkaline earth metals with di-(2-ethylhexyl)orthophosphoric acid (abbreviated as HDEHP). In their study they considered that this fitful phenomenon was caused by the acetate ions present. Thorium has been proved to be a metal subject to the same effect of acetate,11) even in extraction with TTA from acidic solutions. The present author wishes to take this effect into account in clarifying the above phenomenon.

If a divalent metallic cation, M^{2+}, is present in a large excess of acetate ions in the buffer solution, a competition may occur between HT and the acetate ion for co-ordinating to the metal ion in the following manner:

$$M(CH_3COO)^+{}_{(a)} + HT_{(o)} \rightleftharpoons M{\cdot}CH_3COO{\cdot}T_{(o)} + H^+{}_{(a)} \qquad (4)$$

In this case the dependence of the distribution ratio of metal on the hydrogen ion concentration may be written as a first-power dependence. On the

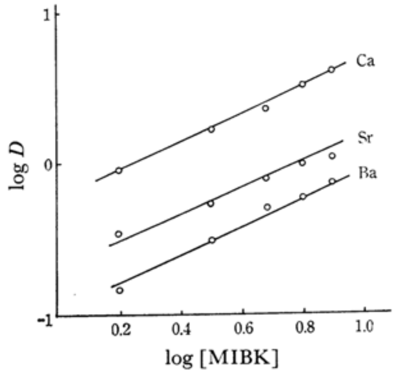

Fig. 11. Dependence of log D to log [MIBK].
Org. phase: 10 ml. of mixed solvent of 0.1 M TTA-MIBK and 0.1 M TTA-benzene in various ratio
Aq. phase: 10 ml. of 0.5 M buffer solution of pH 8.0 containing 0.1 mmol. metal ions

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9) G. K. Schweitzer, *Anal. Chim. Acta*, **30**, 68 (1964).

10) E. Cerrai and G. Ghersini, *J. Chromatog.*, **13**, 211 (1964).

11) G. Goldstein, O. Menis and D. L. Manning, *Anal. Chem.*, **32**, 400 (1960).

TABLE I. SOME ASPECTS OF THE BEHAVIOR OF THE EXTRACTION OF CALCIUM

pH	TTA in organic phase, initial m	Metal ion in aqueous phase, initial, *n*	*x*	m/*n* calcd.	*m*/*n* tangent of the curve in Fig. 10
	M	M			
7.0	0.2	0.0125	1.74	16	8.7
7.0	0.1	0.0125	0.81	8	3.1
7.0	0.05	0.0125	0.36	4	1.95
7.0	0.01	0.0125	0.24	0.8	1.15

other hand, the methyl isobutyl ketone used as an extracting solvent may also participate in the extraction mechanism, because of its polarity. Log *D* and log(MIBK) have a linear relation with a slope of unity, as is shown in Fig. 11, when methyl isobutyl ketone of various concentrations in benzene is used in the extraction of alkaline earth metal from an aqueous solution kept at pH 8 by a 1.0 M buffer solution. This shows that methyl isobutyl ketone can co-ordinate to the alkaline earth metal as a monodentate ligand; therefore, Eqs. 2 and 4 should be revised to 5 and 6, respectively, in such a case:

$$M^{2+}{}_{(a)} + 2HT_{(o)} + L_{(o)} \rightleftharpoons MT_2\cdot L_{(o)} + 2H^+{}_{(a)} \qquad (5)$$

$$M(CH_3COO)^+{}_{(a)} + HT_{(o)} + L_{(o)} \rightleftharpoons MT\cdot CH_3COO\cdot L_{(o)} + H^+{}_{(a)} \qquad (6)$$

where L is methyl isobutyl ketone as a non-charged ligand.

From these equations, the dependence of the distribution ratio on the concentration of TTA is considered to be only linear or quadratic, but the phenomena shown in Fig. 10, in which the distribution ratio increases with the concentration, even by the power of three, cannot be explained unless undissociated TTA is regarded as participating in the equilibrium. Equations 5 and 6, then will become 7 and 8 respectively:

$$M^{2+}{}_{(a)} + (2+m-2)HT_{(o)} + L_{(o)} \rightleftharpoons MT_2(HT)_{m-2}\cdot L_{(o)} + 2H^+{}_{(a)} \qquad (7)$$

$$M(CH_3COO)^+{}_{(a)} + (1+m-1)HT_{(o)} + L_{(o)} \rightleftharpoons MT(HT)_{m-1}\cdot CH_3COO\cdot L_{(o)} + H^+{}_{(a)} \qquad (8)$$

where *m* is the mole number of TTA in the organic phase participating in the extraction and varies with the concentration of TTA added to the system. These equations show the general scheme of the extraction with TTA from an aqueous solution containing metal ions; they satisfactorily explain the phenomena show in Fig. 10. The numerical value 2 noted in Eq. 7 resulted from the extractions carried out in the range of 0.2 M TTA - MIBK and 0.125 mmol. of calcium (cf. Figs. 5—9). Under different conditions each term in Eqs. 7 and 8 may vary with the circumstance and other types of metal chelates may be formed.

In higher concentrations of TTA, the molecules are supposed to associate around the chelate and the distribution of metal may increase remarkably. The acetate ion and methyl isobutyl ketone may be displaced from the chelate by TTA as its concentration increases. For all that, the concentration of TTA plays a principal role in the extraction.

If all of the TTA added in the system reacts with the metal, the equilibrium may be written as follows:

$$nM + (xn + \mathrm{m} - xn)HT \rightleftharpoons n(NT_x\cdot(HT)_{\mathrm{m}/n-x}) + nxH^+ \qquad (9)$$

where n is the moles of metal ion, m is the moles of HT added in the system, and x is the moles of hydrogen ion displaced by the combined HT. From the experimental data on which Figs. 9 and 10 are based, some systematic relations can be derived for the equilibrium of the extraction. These relations are shown in Table I. If all of the TTA present in the system (m) participates in the extraction of all the metal ions (n), the m/n value shown in the fifth column will indicate the number of TTA attachable to a metal ion schematically, but the tangent at any point on the curve in Fig. 10 will indicate the actual number of TTA radicals participating in the extraction of the metal ion at the definite concentrations of TTA and metal ions (sixth column). The number of TTA radicals combined by their ionic linkage in the chelate is given in the column under x. It can be obtained from the slope of the line in the log*D*-pH graph. The conspicuous difference between the values in the fifth and sixth columns from the assumption arbitrarily made in calculating the m/n (the fifth column) that all the TTA is capable of attaching to the metal ion. Therefore, the m in Eq. 9 is not the total concentration of TTA in the system; rather, it should be m, that of the TTA participating in the extraction with the metal. Therefore, the TTA molecules other than those functionally attached seem to be left out of the extraction process. Then, however, the distribution ratio will reach a steady value when the concentration of TTA exceeds some definite value.

However, the distribution ratio shown in Fig. 10 increases boundlessly with the increase in TTA. Therefore, it may be assumed that all the TTA added to the system participates in the extraction in various forms. Then, another equilibrium may be present between the total amount of TTA and the functional amount:

$$\text{total (HT)} \rightleftharpoons m(\text{HT}) \qquad (10)$$

To confirm the above assumption, the following experiment was undertaken. Methyl isobutyl ketone containing 1.48 mol. of TTA per liter was equilibrated with a 0.5 M buffer solution of pH 5.5 of the same volume. The buffer solution thus treated was then used to prepare a solution containing a definite amount of calcium. Each variation in the volume of this solution was taken in a separating funnel, and the total volume was made up to 7.3 ml. with the pre-equilibrated buffer solution. The extraction was carried out between 7.3 ml. of this aqueous solution and the methyl isobutyl ketone pre-equilibrated as above. After the extraction, the amount of calcium ion remaining unextracted was determined by flame-photometry. The ratio of the amount of TTA to that of calcium in the organic phase was calculated from the data obtained over all the range. It was found that when the amount of calcium in the aqueous solution was increased, the calcium in the organic phase reached a saturation point with the molar ratio of calcium to TTA at 1 : 34. In other words, at least thirty-four molecules of TTA were required to extract an ion of calcium. Even this minimum number is larger than the number evaluated from the tangents of the curve of log D-log(TTA) obtained under the same conditions as in this experiment. The number obtained from the curve is considered to be the number of TTA molecules attached to the chelate; apparently, no additional molecules seem to be necessary for the extraction. This is, however, not correct. Since the saturation of calcium occured in the organic solvent when it contained 34 molecules of TTA to one calcium ion and since the distribution ratio of calcium increased boundlessly with the increase in the concentration of TTA, the extra TTA molecules must be regarded as necessary for the extraction. Therefore, it may be supposed that a relatively large number of TTA molecules besides those attached to the chelate are required for the complete extraction of calcium. Consequently, Eq. 10 seems to hold for the equilibrium of the extraction system.

The Separation of Magnesium from Calcium, Strontium and Barium.—The distribution ratios of alkaline earth metals are so close to one another that it seems difficult to separate one from the others, even by multiple-batch extraction. However, if another chelating agent such as EDTA is present in an aqueous solution, calcium may be separated from the others by taking advantage of the greater stability of its EDTA-chelate.

The Behavior of Individual Ions in the Extraction in the Presence of EDTA.—The extraction procedure is based on the principle of competition between TTA and EDTA in the formation of the chelate. To an aqueous solution containing magnesium, calcium, strontium and barium ions and a suitable amount of EDTA, aqueous ammonia was added to make the solution almost neutral; then extraction with TTA-MIBK was carried out as has been previously described. After the extraction the aqueous phase was transferred to a beaker and evaporated nearly to dryness. The residue was dissolved in a mixture of 2 ml. of 6 N hydrochloric acid and 10 ml. of 30% hydrogen peroxide, and then the solution was evaporated nearly to dryness. In order to destroy the EDTA completely, the successive additions of 10 ml. of 30% hydrogen peroxide and evaporations were repeated. After the treatment, some water was added to dissolve the residue; the solution thus obtained was neutralized with sodium hydroxide and then titrated with a standard solution of EDTA, using BT as an indicator, at pH 10.

The extraction with 0.2 M TTA-MIBK was carried out for solutions containing about 0.5 mmol. of each metal ion at varying pH values, in the presence of EDTA in an amount equivalent to the metal. The recovery of the metals, especially calcium and magnesium, in the organic phase is shown in Fig. 12. The result shows that magnesium is very easily extractable, but calcium is not, their separation factor, β, being 139. Further experiments were made in order to examine the behavior of each alkaline earth metal in the presence of as much as four equivalents of EDTA. Table II shows the results obtained in the extraction of magnesium, calcium, strontium and barium at varying pH values. This method was found suitable for separating magnesium from other alkaline earths. EDTA-chelate of calcium has a large stability, but the other metals have a smaller stability. From this fact it may be expected that magnesium, strontium and barium can be extracted all together with TTA; however, this is not the case except for magnesium. This anomalous behavior of strontium and barium may come from the fact that their TTA-chelates have a relatively lower stability than that of magnesium.

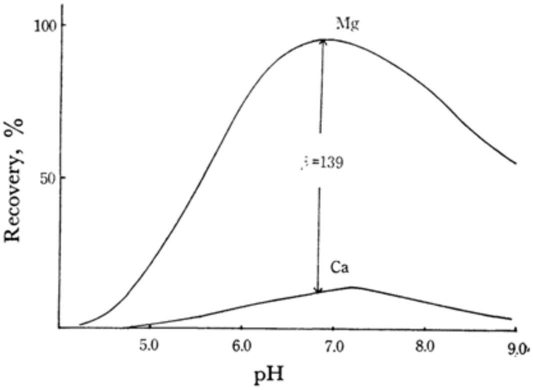

Fig. 12. Behavior of calcium and magnesium in extraction in presence of EDTA.
Taken: Ca 0.52 mmol., Mg 0.42 mmol.
EDTA: 1 : 1 molar ratio to each metal.

TABLE II. BEHAVIOR OF THE ALKALINE EARTH METAL IONS IN EXTRACTION WITH TTA-MIBK IN PRESENCE OF FOUR EQUIVALENTS OF EDTA

Metal ion, taken in 10 ml. of soln.	Final pH	D	% extraction
Mg : 0.42 mmol.	5.6	0.36	26.5
	8.8	0.13	11.9
	6.8	2.71	73.0
	7.4	1.44	59.1
	8.0	0.43	30.4
	8.7	0.17	14.8
Ca : 0.52 mmol.	5.8	0.03	3.6
	6.8	0.03	3.1
	7.8	0.03	3.3
	8.1	0.03	3.0
	8.5	0.02	2.2
	8.7	0.02	2.1
Sr : 0.52 mmol.	5.6	0.04	3.8
	6.1	0.03	3.2
	6.7	0.04	3.9
	7.0	0.03	3.7
	7.5	0.04	4.1
	8.6	0.01	1.5
Ba : 0.50 mmol.	5.5	0.00	0.3
	6.7	0.01	1.0
	8.4	0.01	1.3
	8.9	0.01	1.3

The Separation of Magnesium from Calcium by Extraction with TTA in the Presence of EDTA.—An aqueous solution containing a total amount of magnesium and calcium of 0.5 mmol. was subjected to extraction with 0.2 M TTA-MIBK in the presence of four equivalents of EDTA. The extraction was then repeated two more times with new batches of the organic solvent in order to make a satisfactory separation. The organic phases were then put together into another separating funnel. The back extraction of the organic phase was carried out with 1 N hydrochloric acid. The solution thus obtained was evaporated with the addition of 30% hydrogen peroxide in order to decompose the EDTA. The hydrochloric acid solution was first adjusted to pH 10 by adding a buffer solution of aqueous ammonia and ammonium chloride; then it was titrated with a standard solution of EDTA, using BT as an indicator. The volume of the EDTA solution required was equivalent to the sum of the amounts of calcium and magnesium extracted in the organic phase. Then, another part of the back-extracted solution was treated in the same way, and its pH was adjusted to 12 by adding potassium hydroxide and it was titrated with a standard solution of EDTA, using Dotite NN (calcon) as an indicator. The volume of the EDTA solution required in the latter titration represented the amount of calcium extracted in the organic phase. The recovery of calcium and magnesium from their mixture in various ratios is shown in Table III, from which it may be found that magnesium can be separated largely in the organic phase, while calcium remains in the aqueous phase, although there is some mutual contamination.

TABLE III. SEPARATION OF CALCIUM FROM MAGNESIUM BY EXTRACTION WITH TTA-MIBK IN PRESENCE OF EDTA

Molar ratio in sample soln. Mg : Ca	Recovery in organic phase, % Mg	Ca
Mg alone	95.2	—
2 : 1	95.8	8.7
1 : 2	98.9	8.5
1 : 3	99.5	7.0
Ca alone	—	6.2

Summary

The liquid-liquid extraction of alkaline earth metal ions with 2-thenoyltrifluoroacetone dissolved in methyl isobutyl ketone has been investigated with a view of separating them. The extractability of the ions decreases in the order of magnesium, calcium, strontium and barium; moreover, the distribution ratios between the organic solvent and the aqueous solution are too close to one another for a satisfactory separation. Critical studies have been made on some factors affecting the distribution ratio (hereafter denoted by D) of each metal, such as the amount of metal ion in the aqueous solution, the concentration of TTA in the organic solvent, and the pH of the solution. Among these factors the concentration of TTA in MIBK was found to play a principal role in this extraction, and the relation between $\log D$ and log(TTA) was shown as a curve, not a straight line, in the range of TTA concentration from 0.001 to 0.2 M in MIBK, while another investigators had previously stated that the relation could be shown in many other cases as a straight line with a slope of 2. The slope of the straight line representing the relation between $\log D$ and log (TTA) had usually been believed to show the number of molecules of the chelating agent attached to the metal extracted, i. e., the extracted species; however, the curve obtained by the present author indicates that the extraction process is not so simple but is, rather, very complicated. The difference may be caused by a fact overlooked by the other investigators: the pH of the aqueous solution is lowered enormously by contact with the organic phase, and the distribution ratio is thereby remarkably decreased.

In the author's experiment with 1.48 M TTA-MIBK, the number of TTA molecules attached to a calcium ion is enormously large, at least thirty-four. This phenomenon can be explained

by assuming that, in a lower concentration of TTA, the metal ion is bonded not only by TTA but by the acetate ion present in the buffer solution or by MIBK, a polar solvent, while, on the other hand, in a higher concentration of TTA, the acetate ion and the MIBK do not participate the chelate formation but only the TTA can be attached to the metal, and a network of TTA, which will increase the distribution of metal into the organic solvent, may be produced surrounding the metal.

Among the metal ions, calcium and magnesium could be separated from each other by carrying out the extraction in the presence of EDTA, by virtue of the competition between EDTA and TTA for chelate formation. The author has extended this extraction method to a reversed-phase partition chromatography in a column; this will be described in a following paper.

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